PATENT SPECIFICATION

Convention Date (United States of America): Sept. 10, 1941. **571,494**

Application Date (in United Kingdom): Jan. 31, 1942. No. 1331/42.

Complete Specification Accepted: Aug. 28, 1945.

(Under Section 6 (1) (a) of the Patents &c. (Emergency) Act, 1939, the proviso to Section 91 (4) of the Patents and Designs Acts, 1907 to 1942, became operative on July 11, 1945.)

COMPLETE SPECIFICATION

Rubber Composition

We, WINGFOOT CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of 1144, East Market Street, Akron, Ohio, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a rubber composition containing deproteinized rubber and having greater stiffness and resistance to water absorption than unmodified deproteinized rubber. More particularly, the invention relates to combinations of deproteinized rubber and cyclized rubber in which the properties referred to and others are modified by the presence of the cyclized rubber.

Low protein rubber or, as it is more generally called, deproteinized rubber, is much used in the manufacture of wire and cable insulation and similar products where electrical insulation must be as effective as possible. It is known that rubber from which most of the naturally occurring protein has been removed has a lower water absorption rate than rubber which has not been so treated. However, low protein rubber is very plastic and is difficult to handle in manufacture because it is hard to remove from the mills and does not hold its shape after it has been tubed. In short, the plasticity of this rubber is so great that the material is not easily workable.

It has now been found that the plasticity of deproteinized rubber may be altered to a point where the rubber is readily handled both in milling and tubing operations and, at the same time, the physical properties are improved and the water absorptivity is still further decreased. These beneficial effects are brought about by adding to the low protein rubber a quantity of cyclized rubber, a product resulting from the treatment of natural rubber with tin tetra chloride and the like to alter the arrangement of the rubber molecule to effect a change in the unsaturation without altering the chemical composition. The cyclized rubber is mixed with the deproteinized rubber or a rubber mill or other apparatus, in various proportions as may be indicated by the properties desired in the finished product. Usually the low protein rubber is gradually added to the cyclized rubber, in preference to the reverse procedure.

Compositions of the two rubber hydrocarbons were tested in a stock made up according to the following formula:

	Parts.
Rubber hydrocarbon	100
Zinc oxide	5
Stearic acid	1.5
Lauric acid	1.5
Zinc dimethyl dithiocarbamate	0.2
Mercaptobenzothiazole	1.5
Di-beta-naphthyl-para-phenylene diamine	2.0
Sulfur	1.5

After compound, the stock was cured at a temperature of 300° F. for a period of 1—10 minutes, according to the time required to obtain the best cure. The proportions of deproteinized rubber and of cyclized rubber were varied and physical data obtained was tabulated as follows, water absorption being determined in grams per square inch for 20 hours immersion at 70° C.:

	Tensile Strength	Modulus @ 300%	Elong. at Break	Water Absorption
100 parts deproteinized rubber	3300#	800	800%	.0048
80 D.P. rubber—20 cyclized rubber	3300#	400	610%	.0045
60 D.P. rubber—40 cyclized rubber	2200#	1600	400%	.0038

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It will be noted that in the cured stock the modulus increased and the elongation decreased as the proportion of cyclized rubber was increased, an indication of the stiffening effect of the cyclized rubber while, at the same time, the water absorption had also been reduced. Water absorption is less than that of compounded normal rubber stocks and even less than that of stocks having an all deproteinized rubber base. Of course, it will be understood that a certain amount of plasticity is necessary in a useful product and it is not desired to increase the stiffness beyond a certain point. The cyclized rubber may constitute about 5—50% of the total rubber hydrocarbons present in the stock, i.e., the total rubber present will be made up of 5—50% of cyclized rubber and 95—50% of low protein rubber but, preferably, from 10—35% of cyclized rubber is present. Optimum operating results appear to be obtained when the cyclized rubber constitutes about 20% of the total rubber hydrocarbons.

Other properties of the composition are also altered for the better by the inclusion of the cyclized rubber. Thus, the Shore Durometer hardness of the curved stock rises from an approximate reading of 20 on the Shore type D durometer for 100% deproteinized rubber to approximately 50 for a 50—50 mixture of deproteinized rubber and cyclized rubber. The Shore hardness is an indication of the comparative hardness of the composition. Also, the abrasion resistance is increased by the addition of cyclized rubber, the improvement here being more than one hundred fold, as measured by the amount of material removed under standard condition in a Grasselli Abrasion Machine. Furthermore, the shear resistance, as measured by cutting with a pair of shears, is increased with increase in the cyclized rubber content.

The materials employed in the practice of the invention are well known, but a brief description of them will be given. Deproteinized rubber or, more accurately, low protein rubber, may be prepared by various methods which reduce the nitrogen analysis of the rubber. One method comprises heating rubber latex with caustic alkali, centrifuging repeatedly with dilution of the concentrate between each centrifuging portion, diluting the centrifugal latex and then coagulating. In this method, concentration of the latex may also be effected by creaming, employing a creaming agent such as konnyaku meal, gum tragacanth, iceland moss, etc. Essentially, the method consists in separating serum from the latex after solubilizing the protein thus effecting removal of protein in the serum. Such a deproteinized rubber has a nitrogen analysis of less than 0.1%, as compared with a nitrogen analysis for normal rubber of about 0.4%.

The cyclized rubber may be prepared by heating rubber in the presence of a condensing agent, such as tin tetra chloride or chlorostannic acid. Cyclized rubber is the product resulting from the reaction of rubber with an acid, the negative portion of which acid includes tin and chlorine, the reaction product of rubber with a hydrogenated halogen acid of tin or with a halide of an amphoteric metal. Examples of other reagents which produce cyclized rubber from natural rubber or stannic chloride, ferric chloride, titanium tetra chloride, and chromic chloride. Other known methods and reagents may also be used.

In producing the cyclized rubber, the following procedure, among others may be employed. A rubber cement is diluted with additional solvent and heated for about 2 hours to a temperature of 160° F. Thereafter, the temperature is raised to about 180° F. and 37% hydrochloric acid is added to the extent of about 2.8% of the rubber present. Shortly after, a 50% solution of stannic chloride in benzene is added in amount about 7% of rubber. Water of condensation is progressively withdrawn and the viscosity of the cement is followed until the desired value has been achieved. Thereupon, the reaction is arrested by the addition of cold water directly to the mixture, the cyclized rubber being obtained in solid form. Other methods of preparation, as by heating rubber with phenols and cresols, may also be employed, the foregoing method being given only for the purpose of illustrating the preparation and properties of cyclized rubber.

The improved rubber composition herein described can be easily milled and is readily extrudable from a tubing machine at high speed. Hence, it affords a marked improvement over the deproteinized rubber which has heretofore been used in the extrusion of wire insulation and similar applications. The stiffened composition is also useful in the manufacture of other rubber articles where low moisture absorption and ability to retain the shape imparted is required.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. An improved rubber composition which comprises low protein or deproteinized rubber and cyclized rubber, the

latter being present in an amount of from 5% to 50%, preferably 20% to 50%, by weight, of the total mass.

2. A cured rubber composition which comprises the product obtained by curing an improved composition of the kind claimed in claim 1.

3. An electrical insulation which comprised a cured rubber composition of the kind claimed in claim 2.

Dated this 31st day of January, 1942.

MARKS & CLERK.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1945.

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